

Supporting Information for

Isolation and Reactivity of Trifluoromethyl Iodonium Salts

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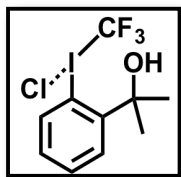
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General considerations

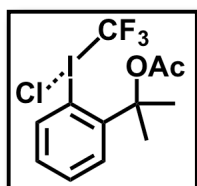
Unless otherwise noted, all commercial reagents were used without further purification. 4-fluorobiphenyl was purified by column chromatography (pentane eluent) prior to use. 2-(2-hydroxyethyl)isoindoline-1,3-dione,¹ Ph₃PAu(4-CH₃-C₆H₄),² and sodium tetrakis(3,5-trifluoromethyl)phenylborate (NaBArF₂₄)³ were prepared according to previously reported procedures. Small-scale reactions were run in conical Eppendorf tubes (1.0 mL). Unless otherwise noted, reactions were conducted without taking precautions to exclude air or moisture. Dichloromethane (CH₂Cl₂) and acetonitrile (MeCN) used in moisture-sensitive reactions were purified by passage through an activated alumina column under argon. Thin-layer chromatography analysis of reaction mixtures was performed using Merck silica gel 60 F254 TLC plates, and visualized under UV or by staining with KMnO₄. Flash column chromatography was carried out on Merck Silica Gel 60 Å, 230 X 400 mesh. Nuclear magnetic resonance (NMR) spectra were recorded using Bruker DRX-500, AVQ-400 and AV-600 spectrometers. ¹H and ¹³C NMR chemical shifts are reported in ppm downfield of tetramethylsilane and referenced to residual solvent peaks. ¹⁹F NMR chemical shifts are reported in ppm relative to CFCl₃ (external standard). ³¹P NMR chemical shifts are reported in ppm relative to phosphoric acid (external standard). Multiplicities are reported using the following abbreviations: s = singlet, d = doublet, t = triplet, q = quartet, m = multiplet, br = broad resonance. Mass spectral data were obtained from the Micro-Mass/Analytical Facility operated by the College of Chemistry, University of California, Berkeley using a Thermo LTQ-FT for ESI spectra and a Waters AutoSpec Premier for EI spectra. X-ray crystallographic data were collected at the University of California, Berkeley College of Chemistry X-ray Crystallography Facility. Cyclic voltammetry experiments (referenced versus Ag/AgNO₃) were conducted in MeCN using tetrabutylammonium hexafluorophosphate (0.1 M) as the electrolyte, a glassy carbon working electrode, and a Pt wire counter electrode. *Caution: we anticipate all iodonium salts could exhibit violent thermal decomposition; due care should be taken when handling or synthesizing these reagents.*

Synthesis of **1•HCl**



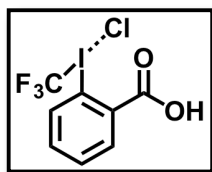
Caution: **1•HCl** was found to decompose violently when heated above 100 °C; due care should be taken when handling or synthesizing this reagent. A 50 mL flask was charged with 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (1.0 g; 3.0 mmol) and CHCl₃ (15 mL). The resultant solution was sparged with HCl gas (generated *ex situ* using NaCl and H₂SO₄) for approximately 5 minutes, after which the reaction mixture was allowed to sit at room temperature for 30 minutes. The mixture was concentrated under reduced pressure and subsequently washed with pentane (3 x 15 mL) to afford **1•HCl** as a white solid (1.05 g; 96% yield). Single crystals of **1•HCl** spontaneously formed from a saturated CDCl₃ solution and were analyzed by X-ray crystallography (see Figure 4 in the main text). ¹H NMR (CDCl₃, 400 MHz, δ): 7.99 (d, *J* = 8.2 Hz, 1H), 7.62-7.53 (m, 2H), 7.36 (t, *J* = 7.7 Hz, 1H), 1.74 (s, 6H). ¹³C{¹H} NMR (CDCl₃, 150.9 MHz δ): 147.6, 135.9, 132.2, 130.4, 128.9, 115.2, 75.1, 31.1 (C_{CF₃} signal not observed due to heteroatom coupling). ¹⁹F NMR (CDCl₃, 376.5 MHz, δ): -27.2 (s). HRMS (ESI) Calc'd for C₁₀H₁₁F₃IO [M-Cl]⁺: 330.9801; found 330.9791.

Synthesis of **1•AcCl**



A 40 mL scintillation vial was charged with **1•HCl** (20.0 mg; 0.05 mmol) and acetyl chloride (2.0 mL; 28.1 mmol). The resultant suspension was sonicated for 5 minutes, after which the reaction mixture was allowed to sit at room temperature for 8 hours. The mixture was concentrated under reduced pressure and subsequently washed with pentane (3 x 5 mL) to afford **1•AcCl** as a white solid (16.7 mg; 75% yield). Single crystals of **1•AcCl** spontaneously grew within the mother liquor during the acylation reaction and were analyzed by X-ray crystallography (see Scheme 2 in the main text). ¹H NMR (CD₂Cl₂, 400 MHz, δ): 8.39 (d, *J* = 7.9 Hz, 1H), 7.74-7.73 (m, 2H), 7.41-7.36 (m, 1H), 2.16 (s, 3H), 2.03 (s, 6H). ¹³C{¹H} NMR (CD₂Cl₂, 150.9 MHz δ): 169.3, 145.5, 141.4, 133.2, 131.1, 129.3, 82.1, 28.3, 22.7 (C_{CF₃} signal not observed due to heteroatom coupling). ¹⁹F NMR (CDCl₃, 376.5 MHz, δ): -31.5 (s). HRMS (ESI) Calc'd for C₁₂H₁₃F₃IO₂ [M-Cl]⁺: 372.9907; found 372.9900.

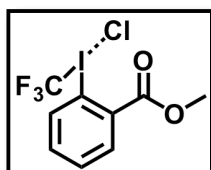
Synthesis of **2•HCl**



Caution: **2•HCl** was found to decompose violently when heated above 100 °C; due care should be taken when handling or synthesizing this reagent. A 100 mL flask was charged with 1-(trifluoromethyl)-1,2-benziodoxol-3-(1H)-one (1.58 g; 5.0 mmol), CH₂Cl₂ (50 mL), and a stir bar. The resultant solution was stirred vigorously and sparged with HCl gas (generated *ex situ* using NaCl and H₂SO₄) for approximately 30 minutes. The precipitated white solid was collected on a fritted funnel and washed with CH₂Cl₂ (3 x 15 mL) to afford **2•HCl** (1.0 g; 57% yield). Single crystals of **2•HCl** formed from a solution in MeCN at -30 °C and were analyzed by X-ray crystallography (see Figure 5 in the main text). ¹H NMR (DMSO-d₆, 600 MHz,

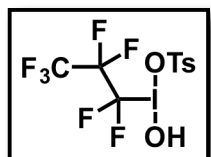
δ): 8.48 (d, $J = 7.9$ Hz, 1H), 8.21 (dd, $J = 7.7, 1.7$ Hz, 1H), 7.82 (t, $J = 7.5$ Hz, 1H), 7.73 (td, $J = 7.7, 1.7$ Hz, 1H). $^{13}\text{C}\{^1\text{H}\}$ NMR (DMSO- d_6 , 150.9 MHz δ): 165.4, 138.5 (m), 135.2, 132.6, 131.7, 130.5, 120.0 (m), 109.2 (q, $J = 389$ Hz). Spectrum shows trace 2-iodobenzoic acid from decomposition during collection. ^{19}F NMR (DMSO- d_6 , 376.5 MHz, δ): -34.3 (s). HRMS (ESI) Calc'd for $\text{C}_8\text{H}_5\text{F}_3\text{IO}_2$ $[\text{M}-\text{Cl}]^+$: 316.9281; found 316.9284.

Synthesis of 2•MeCl



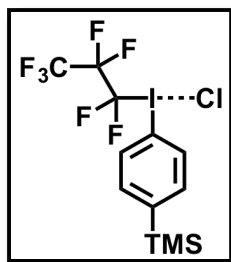
A 50 mL flask was charged with 1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one (0.63 g; 2.0 mmol), CH_2Cl_2 (20 mL), N,N -dimethylformamide (1 drop), and a stir bar. The vessel was placed under a N_2 atmosphere, and oxalyl chloride (1.7 mL; 20 mmol) was added dropwise at room temperature. The reaction mixture was stirred for 30 minutes, after which time the vessel was cooled to 0 °C. Methanol (10 mL) was added in a single portion, and the reaction mixture was immediately concentrated under reduced pressure. Subsequent washing with diethyl ether (3 x 15 mL) afforded **2•MeCl** as a white solid (0.32 g; 43% yield). Single crystals of **2•MeCl** were obtained by vapor diffusion of pentane into a CH_2Cl_2 solution and analyzed by X-ray crystallography (see Scheme 2 in the main text). ^1H NMR (CDCl_3 , 500 MHz, δ): 8.47 (d, $J = 8.0$ Hz, 1H), 8.37-8.33 (m, 1H), 7.79 (t, $J = 7.4$ Hz, 1H), 7.71-7.65 (m, 1H), 4.05 (s, 3H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CDCl_3 , 125 MHz δ): 163.7, 139.5, 135.9, 133.2, 132.6, 128.7, 120.6, 53.6 (C_{CF_3} signal not observed due to heteroatom coupling). ^{19}F NMR (CDCl_3 , 376.5 MHz, δ): -33.4 (s). HRMS (ESI) Calc'd for $\text{C}_9\text{H}_7\text{F}_3\text{IO}_2$ $[\text{M}-\text{Cl}]^+$: 330.9437; found 330.9476.

Synthesis of hydroxy(perfluoropropyl)iodonium tosylate



A 50 mL flask was charged with trifluoroacetic anhydride (11 mL; 78 mmol), trifluoroacetic acid (10 mL; 131 mmol), and a stir bar. The reaction mixture was cooled to 0 °C, and a 30% aqueous solution of hydrogen peroxide (1.2 mL, 12 mmol) was added dropwise. The mixture was then stirred at room temperature for 5 minutes, after which time perfluoropropyl iodide (1.4 mL, 10 mmol) was added slowly. The reaction mixture was stirred for 16 hours at room temperature and then concentrated under reduced pressure (Note: the temperature should be kept below 25°C). The resulting oil was taken up in 40 mL MeCN, and p -toluenesulfonic acid monohydrate (1.90 g; 10 mmol) was added in one portion. The mixture was stirred vigorously at room temperature for 1 hour, and the resulting precipitate was collected by filtration, washed with a small amount of MeCN, and dried in air to yield hydroxy(perfluoropropyl)iodonium tosylate as an off-white solid (1.83 g; 34% yield). Spectroscopic characterization was in agreement with literature reports.⁴

Synthesis of chloro(4-trimethylsilylphenyl)perfluoropropylidone (11)



A 50 mL Schlenk flask was charged with hydroxy(perfluoropropyl)iodonium tosylate (484 mg; 1.0 mmol), 1,4-bis(trimethylsilyl)benzene (400 mg; 1.8 mmol), and a stir bar. The vessel was placed under a N₂ atmosphere, and anhydrous CH₂Cl₂ (15 mL) was added. The reaction mixture was cooled to 0 °C, and BF₃ etherate (220 μL, 12 mmol) was added dropwise. The mixture was then stirred at room temperature for 3 hours, after which time brine (20 mL) was added at 0 °C. The biphasic mixture was stirred several minutes, partitioned, and the aqueous layer was extracted with CH₂Cl₂ (2 x 10 mL). The combined organic layers were dried over magnesium sulfate and concentrated under reduced pressure. The resulting material was taken up in a mixture of diethyl ether/hexanes (1:1 v/v), and the resulting precipitate was collected by filtration, washed with a small amount of hexanes, and dried **11** as a white solid (94 mg; 20% yield). Single crystals of **11** were obtained from a saturated pentane solution at -30 °C and analyzed using X-ray crystallography (see Figure 4 in the main text). ¹H NMR (CDCl₃, 500 MHz, δ): 8.07 (d, *J* = 7.9 Hz, 2H), 7.65 (d, *J* = 7.8 Hz, 2H), 0.32 (s, 9H). ¹³C{¹H} NMR (CDCl₃, 125 MHz δ): 147.7, 136.9, 134.5, 120.3, -1.4 (perfluorinated carbons appear as a set of complex multiplets between 120 and 106). ¹⁹F NMR (CDCl₃, 376.5 MHz, δ): -78.8 (t, *J* = 8.0; 3F), -86.4 (q, *J* = 8.0, 2F), -119.6 (s, 2F). HRMS (ESI) Calc'd for C₁₂H₁₃F₇ISi [M-Cl]⁺: 444.9714; found 444.9710.

Procedures for halide metathesis reactions

1•HF: A 4 dram vial that was wrapped in aluminum foil was charged with **1•HCl** (5.0 mg; 0.01 mmol), AgF (1.7 mg; 0.01 mmol), MeCN (0.5 mL), and a stir bar. The reaction mixture was stirred vigorously for 1 hour, after which the mixture was filtered through a 0.45 μm syringe filter and analyzed by ¹⁹F NMR. The only observed product was 3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole.

In a separate experiment, a 4 dram vial was charged with 3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole (16 mg; 0.05 mmol), triethylamine trihydrofluoride (16 μL; 0.10 mmol), and CH₂Cl₂ (1.0 mL). The reaction mixture was allowed to sit at room temperature for 1 hour, after which time the mixture was analyzed by ¹⁹F NMR. The only observed species was the starting material.

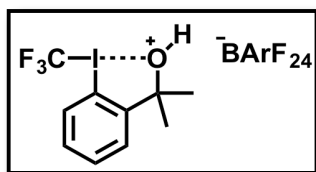
1•HBr: A 4 dram vial was charged with **1•HCl** (20 mg; 0.05 mmol), NaBr (57 mg; 0.5 mmol), acetone (0.5 mL), and a stir bar. The reaction mixture was stirred vigorously for 1 hour, after which the mixture was filtered through a 0.45 μm syringe filter and analyzed by ¹⁹F NMR. CF₃Br, CF₃I, and 3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole were the predominantly observed products.

In a separate experiment, a 50 mL flask was charged with 3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole (95 mg; 0.3 mmol) and CHCl₃ (15 mL). HBr gas (generated *ex situ* using NaBr and H₂SO₄) was bubbled through the resultant solution for approximately 5 minutes at room temperature (Note: the HBr gas was first passed through a CH₂Cl₂ solution of phenol to remove excess Br₂). The reaction mixture was

allowed to sit at room temperature for 30 minutes, after which time the solvent was removed under reduced pressure. ^{19}F NMR analysis revealed a 6:1 mixture of 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole and another product (tentatively assigned as **1•HBr**); however, **1•HBr** decomposed into CF_3Br and CF_3I (along with small amounts of other products that were not identified) upon sitting at room temperature.

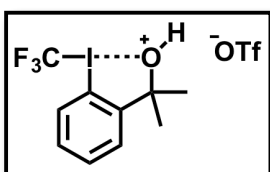
1•HI: A 4 dram vial was charged with **1•HCl** (5.0 mg; 0.01 mmol), NaI (2.0 mg; 0.01 mmol), acetone (0.5 mL), and a stir bar. The reaction mixture was stirred vigorously for 1 hour, after which the mixture was filtered through a 0.45 μm syringe filter and analyzed by ^{19}F NMR. CF_3I , and 3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole were the only observed products.

Synthesis of **1•HBArF₂₄**



In a N_2 filled glove box, a 4 dram vial was charged with **1•HCl** (20 mg; 0.05 mmol), NaBArF_{24} (48 mg; 0.05 mmol), CH_2Cl_2 (2 mL), and a stir bar. The reaction mixture was stirred at room temperature for 5 minutes, after which the mixture was filtered through a 0.45 μm syringe filter and concentrated under reduced pressure. The resulting material was washed with pentane (3 x 5 mL) and dried to afford **1•HBArF₂₄** as a white solid (59 mg; 91% yield). ^1H NMR (CD_2Cl_2 , 400 MHz, δ): 7.74 (br, 9H), 7.66-7.61 (br, 4H), 7.57 (br, 3H), 4.97 (br, 1H), 1.72 (br, 6H). $^{13}\text{C}\{^1\text{H}\}$ NMR (CD_2Cl_2 , 150.9 MHz δ): 161.7 (q, $^1J_{\text{B-C}} = 49.8$ Hz), 145.2, 134.8, 133.6, 133.4, 130.6, 129.9, 128.9 (q, $^2J_{\text{C-F}} = 31.7$ Hz), 124.5 (q, $^1J_{\text{C-F}} = 271$ Hz), 117.5, 107.8, 77.8, 29.5 (C_{CF_3} signal not observed due to heteroatom coupling). ^{19}F NMR (CD_2Cl_2 , 376.5 MHz, δ): -16.6 (s, 3F), -60.1 (s, 24F). HRMS (ESI) Calc'd for $\text{C}_{10}\text{H}_{11}\text{F}_3\text{IO} [\text{M-BArF}_{24}]^+$: 330.9801; found 330.9810.

Synthesis of **1•HOTf**



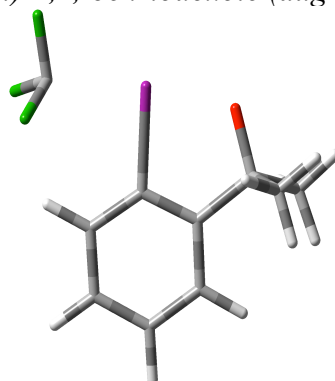
In a N_2 filled glove box, a 4 dram vial was charged with **1•HCl** (20 mg; 0.05 mmol), NaOTf (9.8 mg; 0.05 mmol), CH_2Cl_2 (2 mL), and a stir bar. The reaction mixture was stirred at room temperature for 5 minutes, after which the mixture was filtered through a 0.45 μm syringe filter and analyzed by NMR. ^{19}F NMR (CH_2Cl_2 , 376.5 MHz, δ): -33.3 (s, 3F), -77.9 (s, 3F).

1•HOTf was found to readily decompose in solution (primarily affording CF_3OTf), and the isolated solid was also prone to decomposition. In an attempt to obtain single crystals of **1•HOTf** by slow evaporation of a CH_2Cl_2 solution, we actually obtained **1•HBF₄** (Figure 3). The formation of **1•HBF₄** is attributed to abstraction of boron from the borosilicate glassware used during the crystallization by a decomposition product of **1•HOTf**.

Computational data

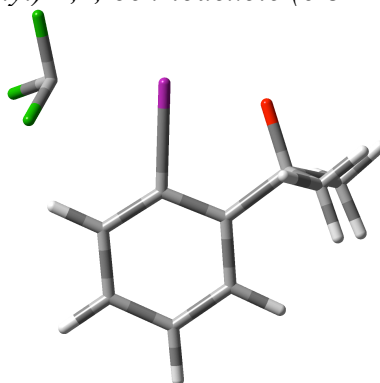
Electronic structure calculations were conducted on 3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole, 1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one, **1•HCl**, and **2•HCl** using Gaussian⁵ at the University of California, Berkeley College of Chemistry Molecular Graphics and Computational Facility. All calculations employed density functional theory and the B3-LYP exchange-correlation energy functional. To ensure that computational results were not qualitatively basis set dependent, both the 6-311+G(d,p) and aug-cc-PVTZ basis sets were used for atoms other than I. An effective core potential (Gaussian code SDD) was used for I. The previously reported crystal structures of 3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole⁶ and 1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one⁷ were used as the initial structures for optimization, with the I–O and I–CF₃ bond lengths constrained to the observed distances in the solid state to facilitate convergence. The crystal structures of **1•HCl** and **2•HCl** reported in this study were used as the initial structures for optimization, with the I–Cl and I–CF₃ bond lengths constrained to the observed distances in the solid state to facilitate convergence. In the case of **2•HCl**, only one of the four inequivalent molecules in the asymmetric unit was selected for computational evaluation. Atom coordinates (in Å) and energies (in Ha) are tabulated below:

3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole (aug-cc-PVTZ; E = -773.45049761)



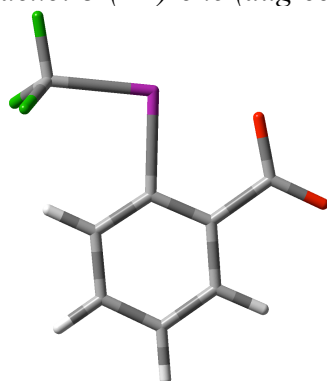
I	0.73262400	-0.92793600	-0.10653800
O	-1.18967700	-1.78669000	-0.33358200
F	2.90077000	1.10813500	-0.96704000
F	2.69803100	1.07910000	1.19284000
F	3.61757600	-0.60190400	0.16581500
C	-0.52849300	0.82265700	-0.07643400
C	-0.05630200	2.12247700	-0.11338400
H	0.99413800	2.35191700	-0.17987700
C	-0.98823100	3.15345300	-0.07261900
H	-0.64760200	4.17875000	-0.10928500
C	-2.34436200	2.86137700	0.01223900
H	-3.06857200	3.66381700	0.04718700
C	-2.77586500	1.54308500	0.04936100
H	-3.83350300	1.33012500	0.11731400
C	-1.86478000	0.48518900	-0.00165000
C	-2.28258500	-0.99353400	0.05211500
C	-2.71629800	-1.34506300	1.48882600
H	-1.90226600	-1.16449300	2.19157800
H	-2.97694700	-2.40241500	1.53096300
H	-3.57878600	-0.75790200	1.80756300
C	-3.42230800	-1.27767400	-0.93677800
H	-3.12044200	-1.00790900	-1.94779200
H	-4.33417900	-0.73617800	-0.68310100
H	-3.64196800	-2.34448000	-0.91713400
C	2.62107500	0.31051300	0.08719600

3,3-dimethyl-1-(trifluoromethyl)-1,2-benziodoxole (6-311+G(d,p); E = -773.35613081)



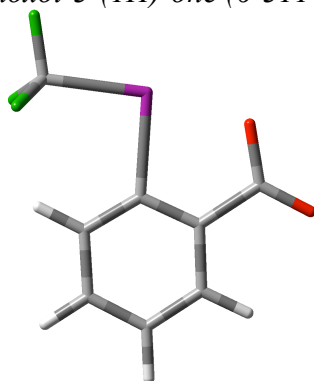
I	0.74888700	-0.93904100	-0.10267700
O	-1.17617900	-1.79088200	-0.33232100
F	2.86558800	1.13967500	-0.97059100
F	2.68311800	1.09198600	1.19598200
F	3.64230400	-0.55793200	0.14810900
C	-0.54481600	0.84210700	-0.07339700
C	-0.07646600	2.14408800	-0.10591600
H	0.97486800	2.38130600	-0.16650600
C	-1.02323200	3.16783400	-0.06923700
H	-0.69193700	4.19901800	-0.10330600
C	-2.38010400	2.85969900	0.00860000
H	-3.11438700	3.65640000	0.04047000
C	-2.80008400	1.53352900	0.04296500
H	-3.85814100	1.30851100	0.10655000
C	-1.87505300	0.48184700	-0.00408000
C	-2.27670600	-1.00814400	0.05104000
C	-2.70597900	-1.36157400	1.49164900
H	-1.89054700	-1.17432300	2.19499400
H	-2.95641100	-2.42396200	1.53360900
H	-3.57523900	-0.78086900	1.81394300
C	-3.41024000	-1.30887500	-0.94370100
H	-3.10621600	-1.03467000	-1.95545100
H	-4.33453800	-0.78131200	-0.69265500
H	-3.61046000	-2.38188100	-0.92406000
C	2.61974000	0.32689900	0.08397000

1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one (aug-cc-PVTZ; $E = -768.86897295$)



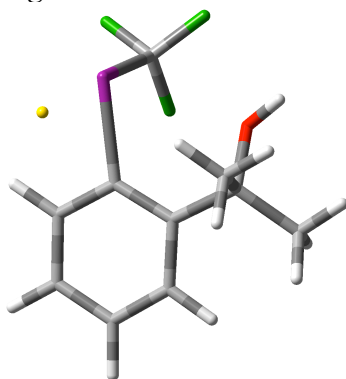
I	-0.70952600	-0.90438300	0.00030300
F	-2.43406800	1.32937500	1.08275800
F	-3.50715100	-0.21767300	0.00010100
F	-2.43328600	1.32775400	-1.08459900
O	3.45205000	-1.85498200	-0.00055600
O	1.22543700	-2.11639100	0.00017000
C	-2.39520400	0.53848900	-0.00011200
C	2.32022500	-1.41380000	-0.00019700
C	2.08353100	0.08513200	-0.00011200
C	0.81379000	0.62572600	0.00024300
C	0.54612700	1.98150900	0.00046300
H	-0.45344600	2.38262100	0.00071700
C	1.63907900	2.84405000	0.00038500
H	1.46397900	3.91086200	0.00059700
C	2.93706400	2.34340600	-0.00002300
H	3.77592000	3.02539900	-0.00010600
C	3.15802700	0.97485300	-0.00030700
H	4.15325100	0.55310300	-0.00056000

1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one (6-311+G(d,p); E = -768.77779561)



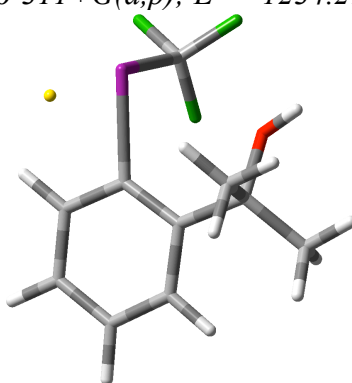
I	-0.73208600	-0.91227400	-0.00018600
F	-2.40671800	1.34900800	1.08605900
F	-3.52790400	-0.16556800	0.00055600
F	-2.40731900	1.34901500	-1.08554900
O	3.44129300	-1.88708500	0.00065000
O	1.20644600	-2.11856500	-0.00041100
C	-2.39423200	0.55764500	0.00020200
C	2.31248400	-1.43683800	0.00012400
C	2.09311900	0.07312600	0.00007200
C	0.83609400	0.64060900	-0.00017500
C	0.57483500	1.99800500	-0.00038400
H	-0.42315100	2.40887900	-0.00067800
C	1.68390100	2.84786300	-0.00028600
H	1.52192100	3.91941700	-0.00049700
C	2.97794500	2.32731600	0.00004500
H	3.82797500	2.99933100	0.00018700
C	3.18181000	0.95227200	0.00021700
H	4.17365000	0.51599400	0.00044900

1•HCl (*aug-cc-PVTZ*; $E = -1234.31263290$)



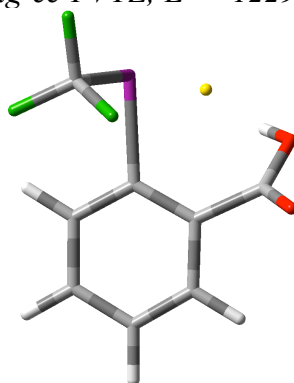
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C	1.76105700	-0.42046200	0.19291100
C	2.91306900	-0.48931000	0.98432100
H	3.77796900	-1.00638600	0.60005100
C	2.99282600	0.07961200	2.24710600
H	3.91113000	-0.00542300	2.81143700
C	1.90434300	0.75012500	2.77913300
H	1.94937200	1.20047300	3.76051800
C	0.74188100	0.84914000	2.02922000
H	-0.10743300	1.38795700	2.41941500
C	1.77489400	-1.02698700	-1.21658500
C	2.03133900	0.07550200	-2.25560100
H	1.98496700	-0.35070700	-3.26096300
H	3.02566200	0.50023600	-2.11954000
H	1.31305700	0.88941000	-2.17868300
C	2.81055200	-2.14679600	-1.37398100
H	2.67437200	-2.91568200	-0.61509200
H	3.83497900	-1.77995100	-1.33557000
H	2.67137600	-2.60692500	-2.35289400
C	-2.01343500	-1.31246200	0.45355200
O	0.47437500	-1.61345800	-1.40540800
H	0.35811300	-1.80825300	-2.34102900
F	-1.18460400	-2.03285700	1.20743100
F	-2.38285100	-2.04946500	-0.60310800
F	-3.12504800	-1.06592900	1.17533800
Cl	0.01104600	3.08519000	-0.97434700
I	-1.18475400	0.63252600	-0.21240000

1•HCl (6-311+G(d,p); $E = -1234.21431071$)



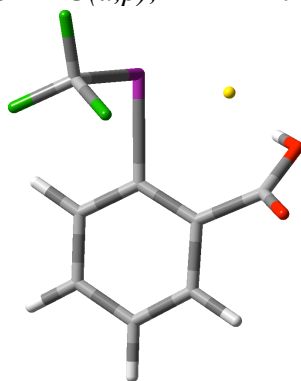
C	0.70043600	0.23003700	0.79948400
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H	3.80525300	-0.98790600	0.52404500
C	3.00947300	-0.03168200	2.25263000
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C	1.91164400	0.58792800	2.83491900
H	1.95449000	0.97056300	3.84737600
C	0.74104500	0.72505600	2.09611100
H	-0.11577100	1.22468300	2.52632200
C	1.79788100	-0.88883500	-1.29288000
C	2.06210200	0.30024900	-2.23454400
H	2.03220900	-0.04022600	-3.27553700
H	3.05397500	0.71876400	-2.04856200
H	1.33484700	1.10220800	-2.09999300
C	2.83437400	-1.99763900	-1.53342500
H	2.68711100	-2.82770700	-0.84023500
H	3.86221000	-1.63824800	-1.45622000
H	2.70376500	-2.37645800	-2.55068000
C	-1.95337800	-1.39299000	0.38870700
O	0.49565800	-1.45413500	-1.53723900
H	0.39392600	-1.59248900	-2.48537000
F	-1.07058400	-2.12756900	1.06733600
F	-2.32945800	-2.07190200	-0.70526200
F	-3.05054900	-1.24342600	1.16172600
Cl	-0.10846500	3.14836500	-0.81196700
I	-1.21855500	0.62170100	-0.17186600

2•HCl (*aug-cc-PVTZ*; $E = -1229.72555675$)



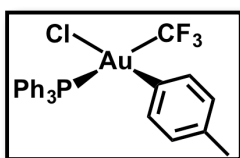
C	-2.25552400	-0.89209300	0.40860200
C	0.70750000	-0.57260300	-0.49521700
C	0.68127400	-1.38174000	-1.62005000
H	-0.12807300	-1.32659700	-2.33137800
C	1.73085400	-2.26911700	-1.81917800
H	1.73079200	-2.90231700	-2.69498200
C	2.76656000	-2.33360100	-0.89652900
H	3.58436500	-3.02416100	-1.04750400
C	2.75815600	-1.51640800	0.22297100
H	3.55049700	-1.57521300	0.95537300
C	1.72975600	-0.59676900	0.44559000
C	1.82390300	0.22779500	1.71353000
O	1.98289400	-0.32628900	2.77095100
O	1.75737000	1.54736800	1.60798700
H	1.69028700	1.90248400	0.67728700
F	-2.44536000	-1.79754200	-0.55388600
F	-3.43558000	-0.34399300	0.71928400
F	-1.76288600	-1.50523800	1.47828700
I	-0.95782900	0.75531300	-0.26501200
Cl	1.15026500	2.70316100	-1.12330200

2•HCl (6-311+G(d,p); E = -1229.62690048)



C	-2.23909300	-0.92114100	0.41273200
C	0.72341800	-0.58439600	-0.49394500
C	0.70681300	-1.39189800	-1.62129300
H	-0.10450000	-1.35396900	-2.33463000
C	1.77981300	-2.25794300	-1.81981300
H	1.79221200	-2.89346700	-2.69701900
C	2.82060000	-2.29792400	-0.89579100
H	3.65498900	-2.97219900	-1.04679200
C	2.79574500	-1.47761300	0.22539900
H	3.59076800	-1.51920800	0.95991300
C	1.74515100	-0.57634100	0.44810900
C	1.81845200	0.24995900	1.72147200
O	1.96000500	-0.30766100	2.78005800
O	1.75553200	1.57074400	1.61616100
H	1.69857700	1.92507300	0.68510700
F	-2.37199000	-1.85139900	-0.53882300
F	-3.44778600	-0.42129100	0.69417800
F	-1.73728800	-1.49333000	1.50224400
I	-0.98623400	0.75575600	-0.27288800
Cl	1.11895600	2.71129300	-1.12075600

Oxidation of $Ph_3PAu(4-CH_3-C_6H_4)$ to $Ph_3PAu(4-CH_3-C_6H_4)(CF_3)(Cl)$



A 4 dram vial wrapped in aluminum foil was charged with $Ph_3PAu(4-CH_3-C_6H_4)$ (12.5 mg; 0.02 mmol), **2**•MeCl (8.3 mg; 0.02 mmol), 4-fluoro-biphenyl (11.7 mg; 0.06 mmol; internal standard), and CD_2Cl_2 (0.5 mL). The reaction was shaken for 2 minutes, and transferred to a foiled NMR tube. ^{19}F and ^{31}P NMR analyses were both consistent² with the formation of the desired Au(III) complex (**12**) as an approximately 1:1 mixture of isomers (42% yield, combined). ^{19}F NMR (CD_2Cl_2 , 376.5 MHz, δ): -29.9 (d, $^3J_{P-F}$ = 68 Hz, *trans*), -28.8 (d, $^3J_{P-F}$ = 45 Hz, *cis*). $^{31}P\{^1H\}$ NMR (CD_2Cl_2 , 161.9 MHz, δ): 23.0 (q, $^3J_{P-F}$ = 69 Hz, *trans*), 36.3 (q, $^3J_{P-F}$ = 44 Hz, *cis*).

In a separate experiment, A 4 dram vial wrapped in aluminum foil was charged with $\text{Ph}_3\text{PAu}(4\text{-CH}_3\text{-C}_6\text{H}_4)$ (12.5 mg; 0.02 mmol), **1•HCl** (8.3 mg; 0.02 mmol), 4-fluoro-biphenyl (11.7 mg; 0.06 mmol; internal standard), and CD_2Cl_2 (0.5 mL). The reaction was shaken for 2 minutes, and transferred to a foiled NMR tube. ^{19}F and ^{31}P NMR analyses were both consistent with the formation of **12** (10% yield). The primary byproducts were determined to be Ph_3PAuCl and 3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole by ^{31}P and ^{19}F NMR, respectively. This suggests that **1•HCl** is sufficiently acidic to preferentially induce protodeauration.

Oxidation of ferrocene to the ferrocenium cation

A 4 dram vial was charged with ferrocene (5.6 mg; 0.03 mmol) and CH_2Cl_2 (400 μL). Two aliquots of the resulting solution (100 μL each) were transferred to two separate 4 dram vials, one containing 1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one (4.8 mg; 0.02 mmol) and the other containing **2•HCl** (5.3 mg; 0.02 mmol). Both reaction mixtures were diluted with CH_2Cl_2 (final volume of 3.0 mL) and stirred at room temperature for 20 minutes. The resulting solutions were filtered through a 0.45 μm syringe filter and analyzed by ultraviolet-visible spectrophotometry (Figure S1A). The reaction between ferrocene and **2•HCl** showed a characteristic absorbance at approximately 620 nm that is consistent⁸ with the formation of ferrocenium. In contrast, the reaction between ferrocene and 1-trifluoromethyl-1,2-benziodoxol-3-(1H)-one showed no absorbance at the aforementioned wavelength.

In a separate experiment, a 4 dram vial was charged with ferrocene (5.6 mg; 0.03 mmol) and CH_2Cl_2 (400 μL). Two aliquots of the resulting solution (100 μL each) were transferred to two separate 4 dram vials, one containing 3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole (7.5 mg; 0.02 mmol) and the other containing **1•HCl** (8.5 mg; 0.02 mmol). Both reaction mixtures were diluted with CH_2Cl_2 (final volume of 3.0 mL) and stirred at room temperature for 20 minutes. The resulting solutions were filtered through a 0.45 μm syringe filter and analyzed by ultraviolet-visible spectrophotometry (Figure S1B). The reaction between ferrocene and **1•HCl** showed a characteristic absorbance at approximately 620 nm that is consistent⁸ with the formation of ferrocenium. In contrast, the reaction between ferrocene and 3,3-dimethyl-1-(trifluoromethyl)-1,2,-benziodoxole showed no absorbance at the aforementioned wavelength.

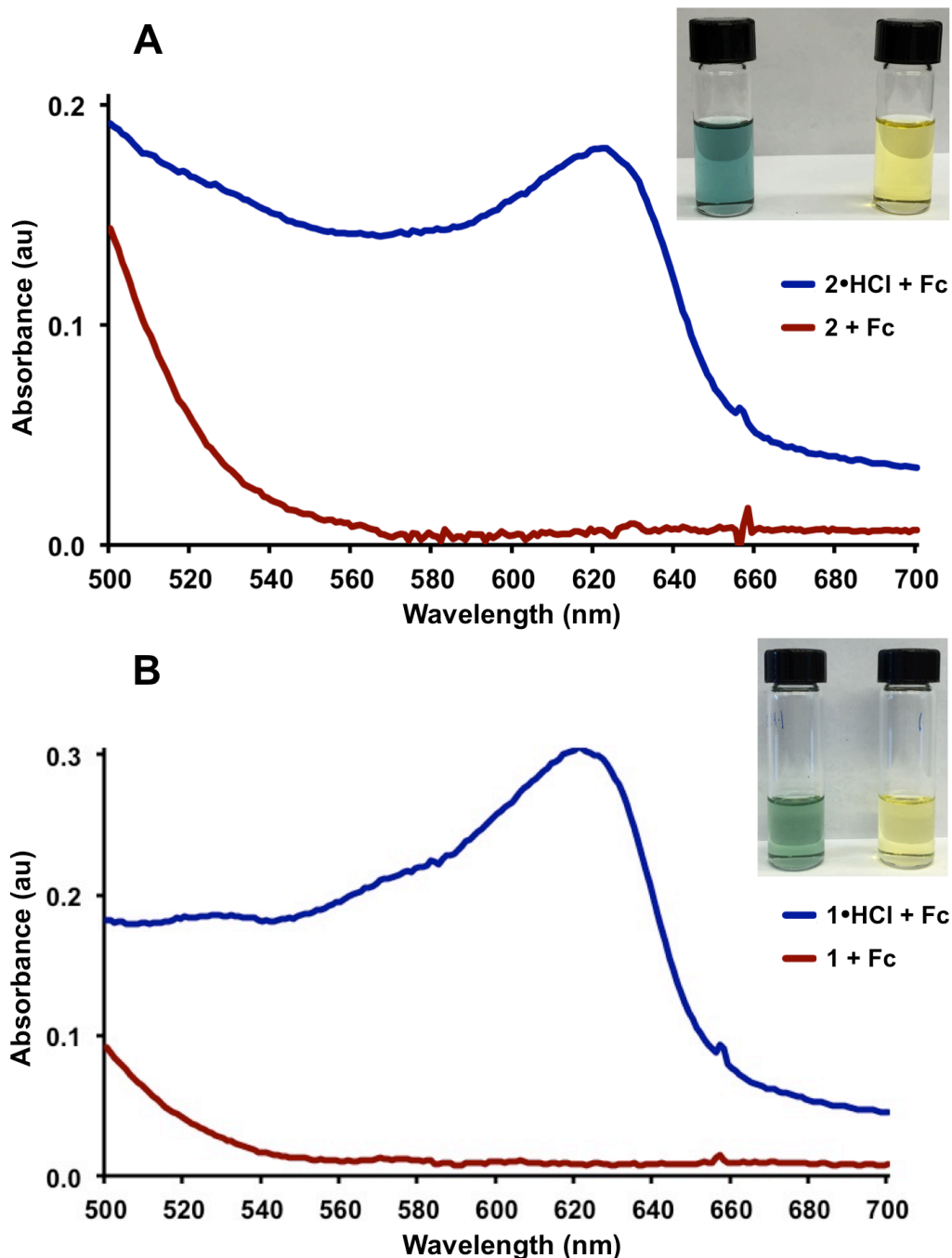
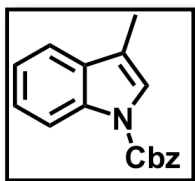


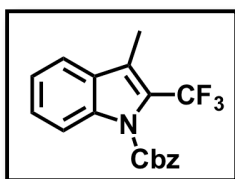
Figure S1. Ultraviolet-visible absorption profiles for ferrocene oxidation products. (A) Ferrocene (Fc) was oxidized to the ferrocenium (Fc^+) cation by $2\bullet\text{HCl}$ (Blue; $[2\bullet\text{HCl}] = 0.007\text{ M}$; CH_2Cl_2). No reaction is observed when the parent iodane (**2**) is reacted with Fc under identical conditions (Red; $[2] = 0.007\text{ M}$; CH_2Cl_2). The inset photograph shows the crude reaction mixtures using $2\bullet\text{HCl}$ (left) and **2** (right). (B) Fc was oxidized to Fc^+ by $1\bullet\text{HCl}$ (Blue; $[1\bullet\text{HCl}] = 0.007\text{ M}$; CH_2Cl_2). No reaction is observed when the parent iodane (**1**) is reacted with Fc under identical conditions (Red; $[1] = 0.007\text{ M}$; CH_2Cl_2). The inset photograph shows the crude reaction mixtures using $1\bullet\text{HCl}$ (left) and **1** (right).

Synthesis of benzyl 3-methyl-1H-indole-1-carboxylate



A 50 mL flask was charged with 3-methylindole (656 mg; 5.0 mmol), sodium hydroxide (600 mg; 15 mmol), tetrabutylammonium bisulfate (85 mg; 0.35 mmol), CH₂Cl₂ (25 mL), and a stir bar. The suspension was stirred at room temperature for 1 hour, after which the mixture was cooled to 0 °C and benzyl chloroformate (1.4 mL; 10 mmol) was added dropwise. The mixture was stirred for 16 hours at room temperature, then partitioned between CH₂Cl₂ and saturated aqueous ammonium chloride. The aqueous layer was extracted with CH₂Cl₂ (2 x 15 mL), and the combined organic layers were washed with brine, dried over magnesium sulfate, and concentrated under reduced pressure. The resulting residue was purified by silica chromatography (5-7% ethyl acetate/hexanes eluent) to afford the desired product (**20**) as a pale orange oil (1.18 g; 89%). ¹H NMR (CDCl₃, 600 MHz, δ): 8.20 (br, 1H), 7.54-7.49 (m, 3H), 7.45-7.38 (m, 4H), 7.37-7.33 (m, 1H), 7.31-7.27 (m, 1H), 5.46 (s, 2H), 2.28 (s, 3H). ¹³C{¹H} NMR (CDCl₃, 150.9 MHz δ): 150.8, 135.6, 135.3, 131.5, 128.7, 128.6, 128.4, 124.5, 122.7, 122.3, 119.0, 117.3, 115.2, 68.4, 9.6. HRMS (EI) Calc'd for C₁₇H₁₅NO₂ [M]⁺: 265.1103; found 265.1106.

Trifluoromethylation of benzyl 3-methyl-1H-indole-1-carboxylate



A conical plastic tube was charged with **2**•HCl (70 mg; 0.20 mmol), benzyl 3-methyl-1H-indole-1-carboxylate (80 mg; 0.30 mmol), CHCl₃ (400 μL), and a stir bar. The reaction mixture was stirred at 60 °C for 3 hours, after which the reaction was diluted with CH₂Cl₂ (5 mL) and extracted with saturated aqueous sodium bicarbonate. The organic layer was dried over magnesium sulfate, concentrated, and purified by silica chromatography (10-30% CH₂Cl₂/hexanes eluent) to afford the desired product (**21**) as a colorless oil (33 mg; 49% yield). Benzyl 3-methyl-1H-indole-1-carboxylate (31 mg; 39% yield) could be recovered by further elution. ¹H NMR (CDCl₃, 300 MHz, δ): 8.13 (d, *J* = 8.5 Hz, 1H), 7.60 (d, *J* = 7.9 Hz, 1H), 7.53-7.36 (m, 6H), 7.31 (t, *J* = 7.5 Hz, 1H), 5.46 (s, 2H), 2.45 (q, *J* = 3.0 Hz, 3H). ¹³C{¹H} NMR (CDCl₃, 125 MHz δ): 150.4, 136.5, 134.5, 129.0, 128.89, 128.85, 128.7, 127.6, 124.1 (q, *J* = 2.8 Hz), 123.5, 122.7, 120.1, 115.8, 122.2 (q, *J* = 37.6 Hz), 69.6, 9.7 (q, *J* = 3.4 Hz). ¹⁹F NMR (CDCl₃, 376.5 MHz, δ): -53.9 (s). HRMS (EI) Calc'd for C₁₈H₁₄F₃NO₂ [M]⁺: 330.0977; found 330.980.

Representative procedure for alcohol trifluoromethylation

A conical plastic tube was charged with 2-(2-hydroxyethyl)isoindoline-1,3-dione (39.5 mg; 0.20 mmol), **1**•HCl (25.0 mg; 0.07 mmol), NaBARF₂₄ (6.0 mg; 0.007 mmol) and MeCN (140 μL). The suspension was heated at 55 °C with stirring for 16 hours, after which the reaction mixture was filtered through a 0.45 μm syringe filter and loaded onto a silica column. Elution with 30% diethyl ether in pentane afforded the desired product (**15g**) as a colorless solid (4.0 mg; 23% yield). Spectroscopic characterization was in agreement with literature⁹ reports. The remaining products shown in Table 1 were

prepared using an analogous procedure; product yields (which are an average of at least two independent experiments) were determined using ^{19}F NMR with 4-fluoro-biphenyl as an internal standard. ^{19}F NMR chemical shifts were consistent^{9,10} with previous literature reports and are tabulated below [^{19}F NMR (CD_2Cl_2 , 376.5 MHz, δ)]:

15a: -59.7 (s)

15b: -60.9 (s)

15c: -61.1 (s)

15d: -59.9 (s)

15e: -60.1 (s)

15f: -59.7 (s)

15g: -60.1 (s)

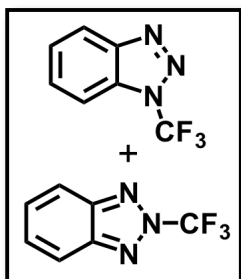
15h: -56.8 (s)

15i: -60.3 (s)

In a separate experiment, a conical plastic tube was charged with 1-adamantanemethanol (10.0 mg; 0.060 mmol), **1•HBArF₂₄** (3.3 mg; 0.003 mmol), 4-fluoro-biphenyl (1.5 mg; 0.009 mmol) and MeCN (55 μL). The suspension was heated at 55 °C for 16 hours, after which the reaction mixture was analyzed by ^{19}F NMR. The product (**15a**) was observed in 35% yield.

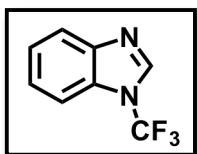
1•HCl and **2•HCl** could also be used directly for alcohol trifluoromethylations under solvolytic conditions. In one experiment, a plastic conical tube was charged with **1•HCl** (5.0 mg; 0.013 mmol), 4-fluoro-biphenyl (7.0 mg; 0.041 mmol), and 3-phenyl-1-propanol (0.5 mL). The mixture was heated at 55 °C for 16 hours, after which the reaction was analyzed by ^{19}F NMR. The desired product (**15f**) was observed in 75% yield. In a separate experiment, a plastic conical tube was charged with **2•HCl** (5.0 mg; 0.014 mmol), 4-fluoro-biphenyl (7.3 mg; 0.042 mmol), and 3-phenyl-1-propanol (0.5 mL). The mixture was heated at 55 °C for 16 hours, after which the reaction was analyzed by ^{19}F NMR. The desired product (**15f**) was observed in 70% yield.

Trifluoromethylation of benzotriazole



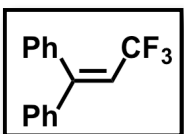
A conical plastic tube was charged with benzotriazole (10.0 mg; 0.08 mmol), **1•HCl** (10.0 mg; 0.03 mmol), NaBArF₂₄ (2.4 mg; 0.003 mmol), 4-fluoro-biphenyl (4.7 mg; 0.03 mmol), and CH_2Cl_2 (55 μL). The suspension was heated at 55 °C for 16 hours, after which time the reaction mixture was analyzed by ^{19}F NMR. The desired products (**17a** and **17b**) were obtained in 59% combined yield. ^{19}F NMR (CD_2Cl_2 , 376.5 MHz, δ): -57.0 (s; **17a**), -60.0 (s; **17b**). Spectroscopic data were in agreement with previous literature reports.¹¹

Trifluoromethylation of benimidazole



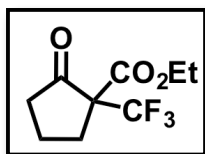
A conical plastic tube was charged with benzimidazole (5.0 mg; 0.04 mmol), **2•MeCl** (5.0 mg; 0.01 mmol), NaBArF₂₄ (1.2 mg; 0.001 mmol), 4-fluoro-biphenyl (2.3 mg; 0.01 mmol), and MeCN (27 μ L). The suspension was heated at 55 °C for 16 hours, after which time the reaction mixture was analyzed by ¹⁹F NMR. The desired product (**19**) was obtained in 41% yield. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz, δ): -56.9 (s). Spectroscopic data were in agreement with previous literature reports.¹²

Trifluoromethylation of 1,1-diphenyl ethylene



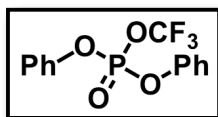
A conical plastic tube was charged with diphenylethylene (27 mg; 0.15 mmol), **2•HCl** (17.6 mg; 0.050 mmol), p-fluorobiphenyl (25.8 mg; 0.15 mmol), and CDCl₃ (200 μ l). The reaction mixture was heated at 60 °C for 16 hours. Analysis by ¹⁹F NMR indicated formation of the desired product (**23**) in 37% yield. ¹⁹F NMR (CDCl₃, 376.5 MHz, δ): -55.2 (d, $J = 8.4$ Hz). Spectral data are in agreement with literature reports.¹³

Trifluoromethylation of 2-ethoxycarbonyl-1-cyclopentanone



A 1 dram vial was charged with potassium 2-ethoxycarbonyl-1-cyclopentanone (9.7 mg; 0.06 mmol), p-fluorobiphenyl (25.8 mg; 0.15 mmol), CD₂Cl₂ (1.0 mL), and a stir bar. To the suspension was added **2•MeCl** (18.3 mg; 0.05 mmol), and the mixture stirred at room temperature for 2 hours. The mixture was filtered through celite, and analysis by ¹⁹F NMR indicated the formation of the desired product (**25**) in 22% yield. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz, δ): -68.4 (s). Spectral data are in agreement with literature reports.¹⁴

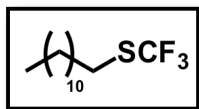
Trifluoromethylation of diphenylphosphate



A 1 dram vial was charged with potassium diphenyl phosphate (14.4 mg, 0.050 mmol), **2•MeCl** (18.3 mg, 0.050 mmol), p-fluorobiphenyl (25.8 mg, 0.15 mmol), and a stir bar. The solids were suspended in CD₂Cl₂ (1.0 mL) and stirred at room temperature for 2 hours. The reaction mixture was filtered through a plug of celite and analyzed by ¹⁹F NMR, which indicated the desired product (**27**) was present in 45% yield. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz, δ): -52.0 (d; ³ $J_{P-F} = 4.6$ Hz). Diphenyl fluorophosphate was also observed in 12% yield. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz, δ): -77.3 (d; $J_{P-F} = 1001$ Hz).

In a separate experiment, a 1 dram vial was charged with diphenylphosphoric acid (12.5 mg, 0.050 mmol), **2•MeCl** (18.3 mg, 0.050 mmol), p-fluorobiphenyl (25.8 mg, 0.15 mmol), and a stir bar. The solids were suspended in CD₂Cl₂ (1.0 mL) and stirred at room temperature for 16 hours. The reaction mixture was filtered through a plug of celite and analyzed by ¹⁹F NMR, which indicated that the desired product was formed in 6% yield.

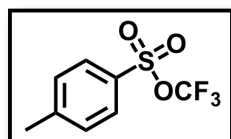
Trifluoromethylation of dodecanethiol



A 10 mL Schlenk flask was charged with sodium hydride (6.7 mg of a 60% suspension in mineral oil; ~0.2 mmol) and a stir bar. The flask was evacuated and backfilled with N₂ (3 x), and dry MeCN (2.0 mL) was added. The vessel was cooled to 0 °C, and dodecanethiol (20 μL; 0.2 mmol) was added under a countercurrent of N₂. The resulting suspension was stirred at 0 °C for 10 minutes, and then room temperature for an additional 30 minutes. **2•MeCl** (10.0 mg; 0.027 mmol) was added under a countercurrent of N₂, and the resulting mixture was stirred at room temperature for 16 hours. 4-fluoro-biphenyl (14.0 mg; 0.08 mmol) was added, an aliquot of the mixture (0.5 mL) was diluted with CD₂Cl₂ and analyzed by ¹⁹F NMR. The desired product (**29**) was observed in 95% yield. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz, δ): -41.2 (s). Spectral data are in agreement with literature reports.¹⁵

In a separate experiment, a 1 dram vial was charged with dodecanethiol (10.1 mg, 0.050 mmol), **2•MeCl** (18.3 mg, 0.050 mmol), p-fluorobiphenyl (25.8 mg, 0.15 mmol), and a stir bar. The reactants were dissolved in CD₃CN (1.0 mL) and stirred at room temperature for 16 hours. No formation of the desired product was observed by ¹⁹F NMR.

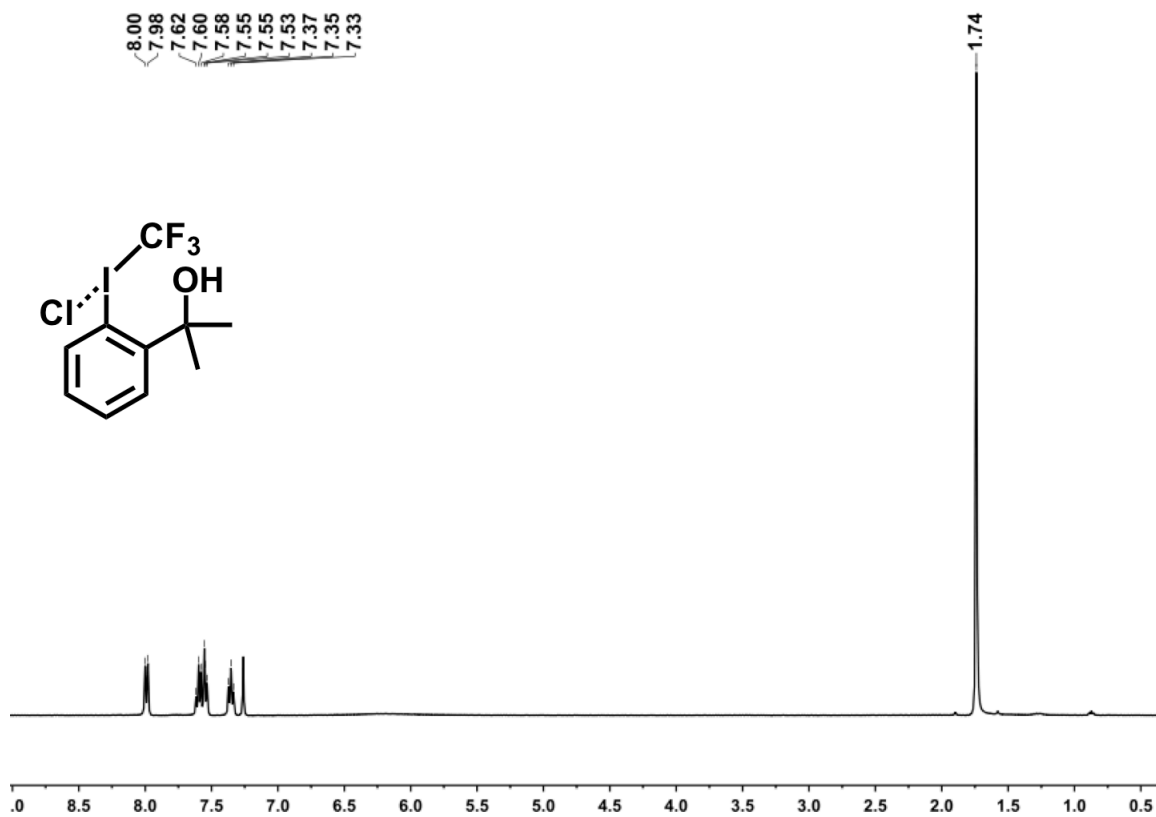
Trifluoromethylation of p-toluenesulfonate

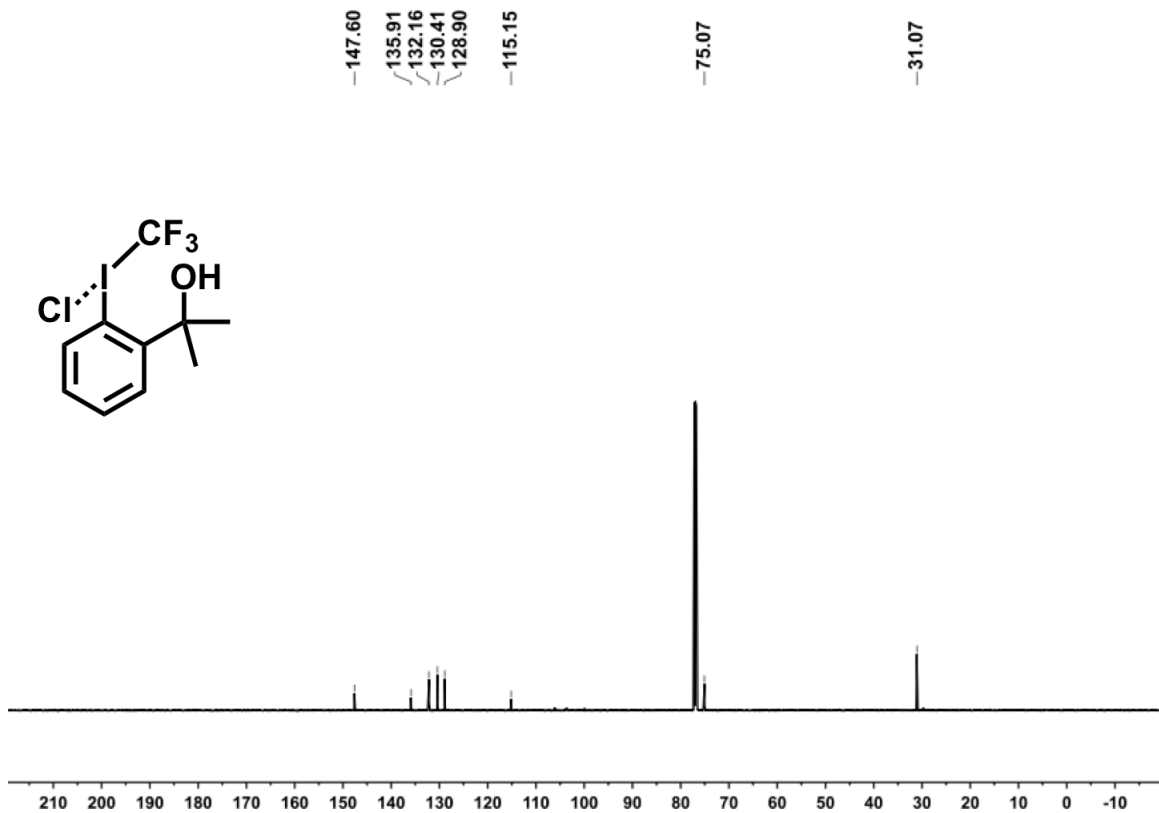


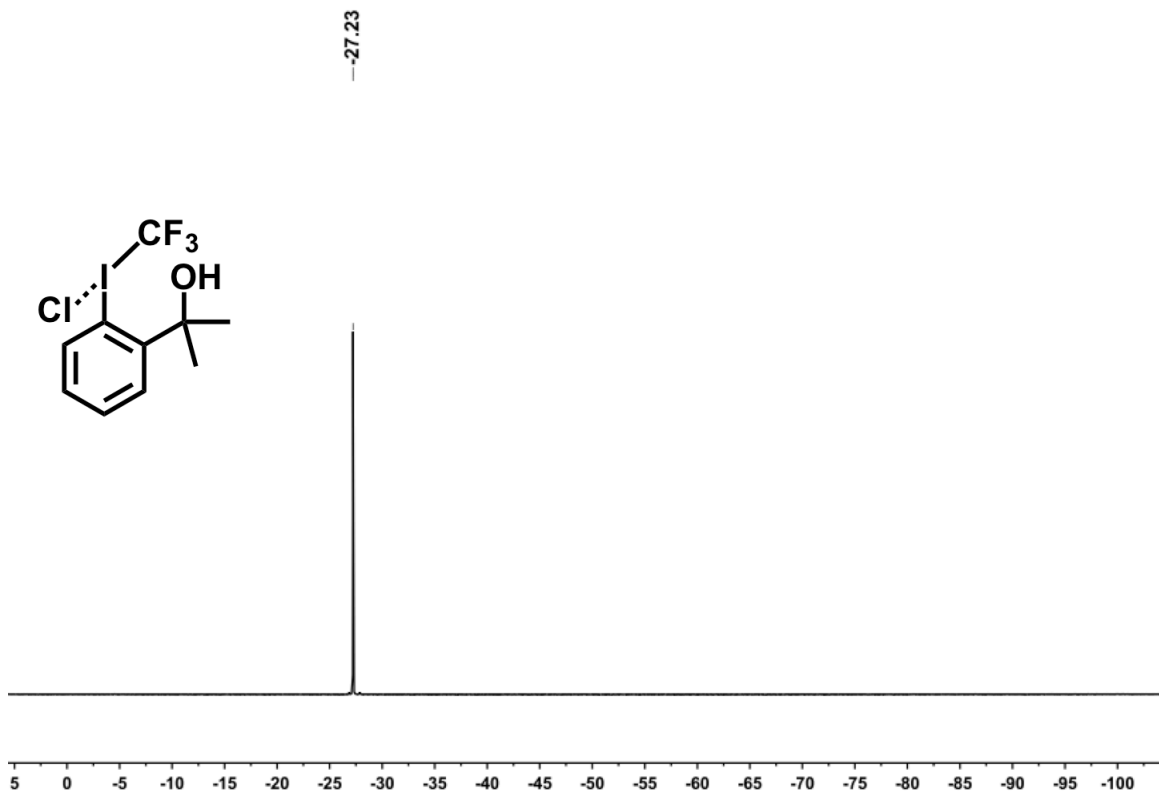
A 1 dram vial was charged with sodium p-toluenesulfonate (9.7 mg, 0.050 mmol), **2•MeCl** (18.3 mg, 0.050 mmol), p-fluorobiphenyl (25.8 mg, 0.15 mmol), and a stir bar. The solids were suspended in CD₂Cl₂ (1.0 mL) and stirred at room temperature for 16 hours. The reaction mixture was filtered through a plug of celite and analyzed by ¹⁹F NMR, which indicated that the desired product (**31**) was formed in 70% yield. ¹⁹F NMR (CD₂Cl₂, 376.5 MHz, δ): -53.6 (s). Spectral data were in agreement with previous reports.¹⁶

In a separate experiment, a 1 dram vial was charged with p-toluenesulfonic acid monohydrate (9.5 mg, 0.050 mmol), **2•MeCl** (18.3 mg, 0.050 mmol), p-fluorobiphenyl (25.8 mg, 0.15 mmol), and a stir bar. The solids were suspended in CD₂Cl₂ (1.0 mL) and stirred at room temperature for 16 hours. The reaction mixture was analyzed by ¹⁹F NMR, which indicated that **31** was formed in 78% yield.

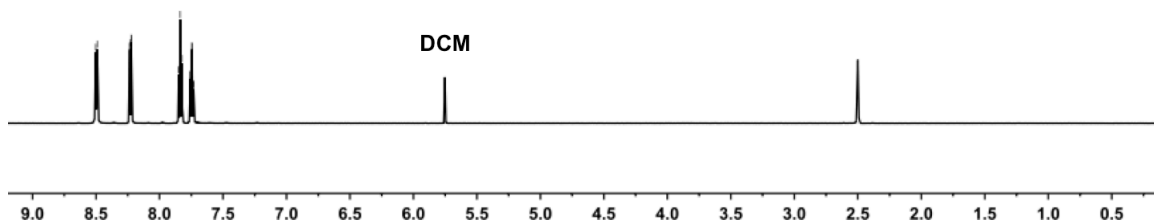
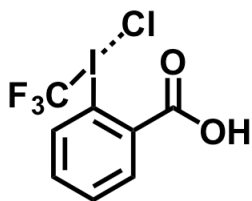
NMR spectra

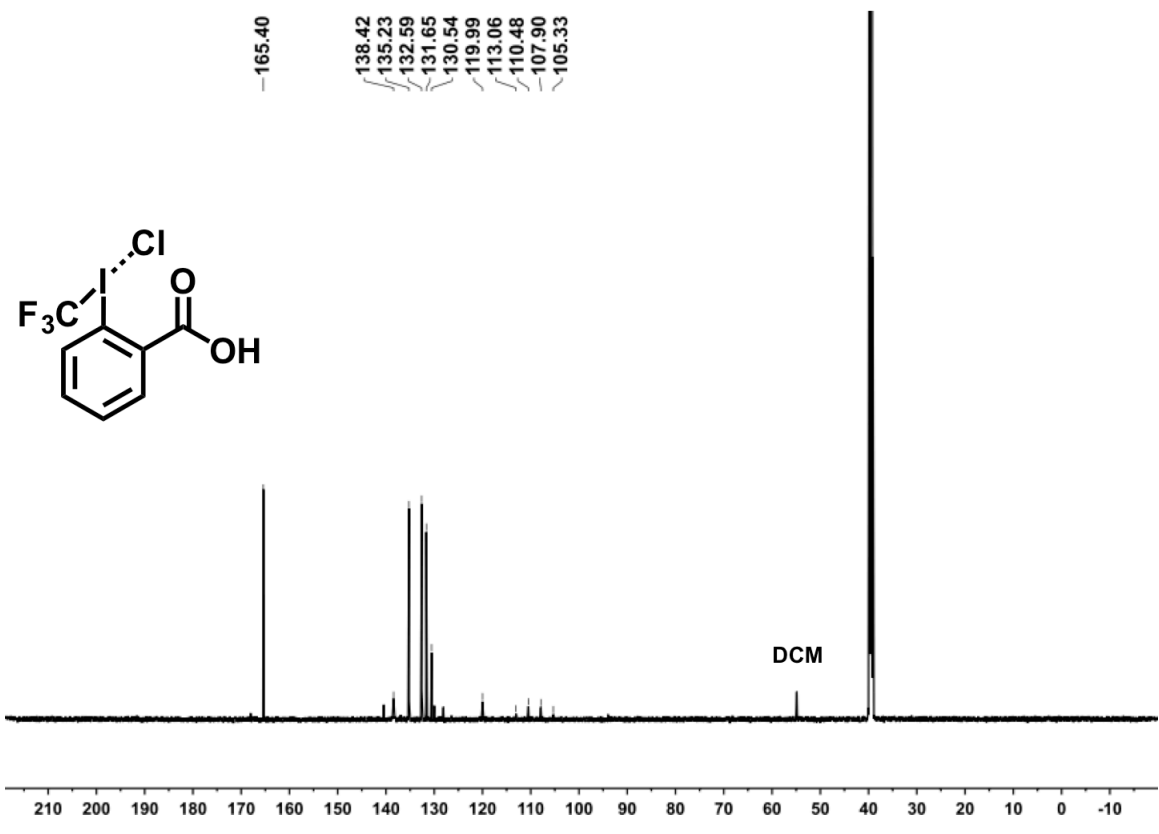


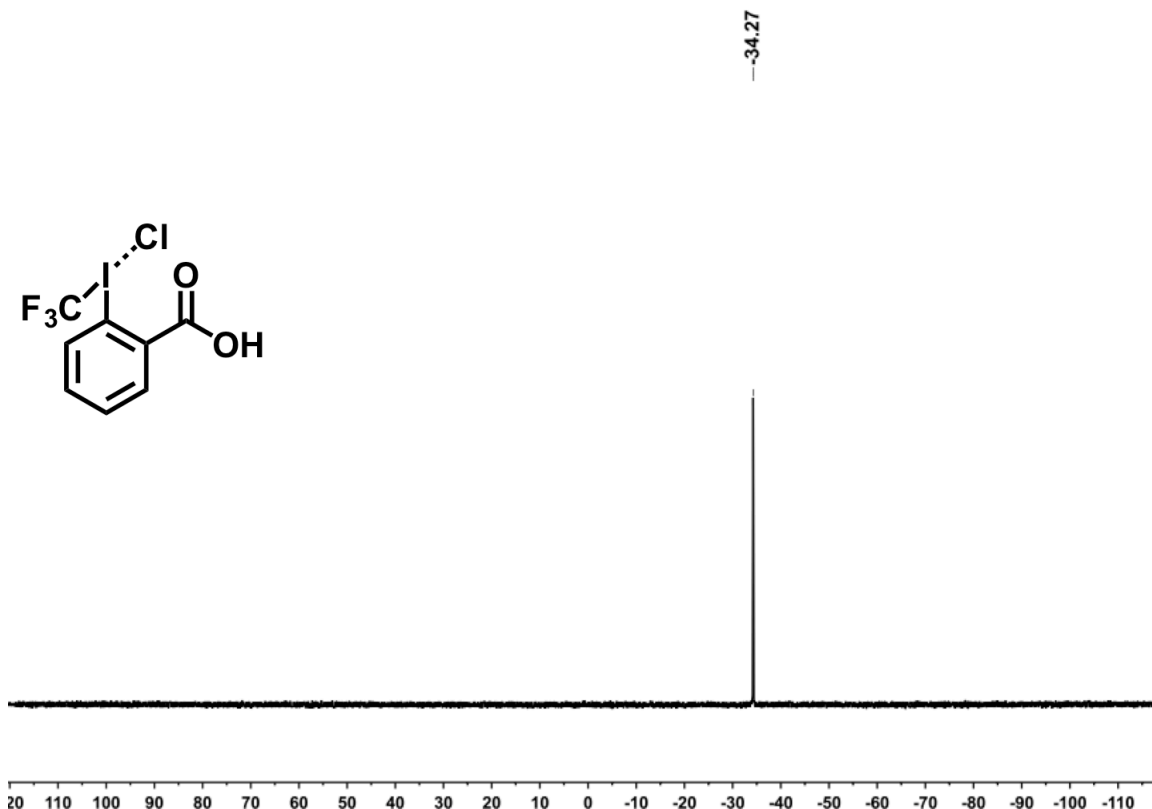




8.50
8.49
8.24
8.23
8.22
8.22
7.85
7.84
7.76
7.76
7.75
7.74
7.73







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Crystallographic data

Table 1. Crystal data and structure refinement for **1•HBF₄**

Identification code	shelx	
Empirical formula	C10 H11 B F7 I O S0	
Formula weight	417.90	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 15.9890(9) Å	a = 90°.
	b = 8.7606(5) Å	b = 93.788(3)°.
	c = 19.0524(11) Å	g = 90°.
Volume	2662.9(3) Å ³	
Z	8	
Density (calculated)	2.085 Mg/m ³	
Absorption coefficient	2.479 mm ⁻¹	
F(000)	1600	
Crystal size	0.060 x 0.020 x 0.020 mm ³	
Theta range for data collection	1.276 to 25.396°.	
Index ranges	-19<=h<=19, -10<=k<=10, -22<=l<=22	
Reflections collected	75792	
Independent reflections	4884 [R(int) = 0.0489]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.688	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	4884 / 0 / 361	
Goodness-of-fit on F ²	1.092	
Final R indices [I>2sigma(I)]	R1 = 0.0480, wR2 = 0.1144	
R indices (all data)	R1 = 0.0565, wR2 = 0.1200	
Extinction coefficient	n/a	
Largest diff. peak and hole	3.333 and -1.095 e.Å ⁻³	

Table 2. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1•HBF₄**. U(eq) is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	8832(3)	1807(6)	4500(3)	21(1)
C(2)	9612(3)	3449(5)	5902(3)	15(1)
C(3)	10313(3)	3265(6)	5525(3)	19(1)
C(4)	11098(3)	3474(6)	5877(3)	23(1)
C(5)	11152(3)	3844(6)	6579(3)	21(1)
C(6)	10433(3)	4023(6)	6946(3)	19(1)
C(7)	9637(3)	3855(5)	6612(3)	15(1)
C(8)	8845(3)	4067(6)	7008(3)	17(1)
C(9)	8551(3)	2542(6)	7288(3)	21(1)
C(10)	8948(3)	5250(6)	7585(3)	26(1)
C(11)	6198(3)	6979(6)	5403(3)	24(1)
C(12)	5379(3)	8572(6)	4002(3)	15(1)
C(13)	4673(3)	8406(6)	4376(3)	18(1)
C(14)	3895(3)	8571(6)	4016(3)	22(1)
C(15)	3841(3)	8931(6)	3306(3)	20(1)
C(16)	4571(3)	9089(5)	2946(3)	17(1)
C(17)	5360(3)	8924(5)	3289(3)	14(1)
C(18)	6160(3)	9085(6)	2895(2)	16(1)
C(19)	6050(3)	10148(6)	2263(3)	22(1)
C(20)	6464(3)	7521(6)	2678(3)	19(1)
O(1)	8182(2)	4582(4)	6501(2)	21(1)
O(2)	6796(2)	9716(4)	3390(2)	19(1)
F(1)	9333(2)	708(4)	4725(2)	28(1)
F(2)	9210(2)	2666(4)	4049(2)	30(1)
F(3)	8148(2)	1217(4)	4175(2)	35(1)
F(4)	5819(2)	7761(4)	5879(2)	32(1)
F(5)	6897(2)	6397(4)	5696(2)	38(1)
F(6)	5703(2)	5876(4)	5165(2)	28(1)
F(7)	8724(2)	7222(4)	5918(2)	46(1)
F(8)	8055(2)	8598(5)	6700(2)	48(1)

F(9)	7956(2)	9266(4)	5561(2)	49(1)
F(10)	9180(2)	9591(4)	6209(2)	29(1)
F(11)	5787(2)	4277(5)	3838(2)	51(1)
F(12)	6569(3)	2538(5)	4488(2)	59(1)
F(13)	6780(2)	2865(4)	3340(2)	34(1)
F(14)	7136(2)	4689(5)	4134(2)	56(1)
I(1)	8407(1)	3185(1)	5377(1)	19(1)
I(2)	6581(1)	8451(1)	4543(1)	19(1)
B(1)	8469(4)	8679(7)	6099(3)	19(1)
B(2)	6553(4)	3591(7)	3950(3)	19(1)

Table 3. Crystal data and structure refinement for **5**.

Identification code	shelx	
Empirical formula	C ₁₂ H ₁₃ Cl F ₇ I Si	
Formula weight	480.66	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 12.0089(4) Å	a = 90°.
	b = 25.0752(9) Å	b = 115.4650(10)°.
	c = 12.5156(4) Å	g = 90°.
Volume	3402.6(2) Å ³	
Z	8	
Density (calculated)	1.877 Mg/m ³	
Absorption coefficient	2.169 mm ⁻¹	
F(000)	1856	
Crystal size	0.100 x 0.060 x 0.030 mm ³	
Theta range for data collection	1.624 to 25.384°.	
Index ranges	-13 ≤ h ≤ 14, -30 ≤ k ≤ 25, -15 ≤ l ≤ 14	
Reflections collected	39280	
Independent reflections	6244 [R(int) = 0.0385]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.642	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	6244 / 0 / 403	
Goodness-of-fit on F ²	1.095	
Final R indices [I > 2σ(I)]	R1 = 0.0246, wR2 = 0.0561	
R indices (all data)	R1 = 0.0263, wR2 = 0.0569	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.055 and -0.603 e.Å ⁻³	

Table 4. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **5**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U^{ij} tensor.

	x	y	z	U(eq)
C(1)	5766(3)	4566(1)	2339(3)	22(1)
C(2)	5770(3)	4317(1)	3453(2)	24(1)
C(3)	6833(3)	3926(1)	4144(3)	29(1)
C(4)	4840(2)	5750(1)	2147(2)	19(1)
C(5)	5528(3)	6034(1)	1703(2)	22(1)
C(6)	5982(2)	6526(1)	2198(2)	22(1)
C(7)	5767(2)	6740(1)	3128(2)	18(1)
C(8)	5072(3)	6427(1)	3549(2)	24(1)
C(9)	4601(3)	5934(1)	3067(2)	23(1)
C(10)	5074(3)	7738(1)	4059(3)	28(1)
C(11)	6564(3)	7818(1)	2609(2)	25(1)
C(12)	7744(3)	7376(1)	5154(2)	23(1)
C(13)	9032(3)	5047(1)	7518(2)	22(1)
C(14)	9263(3)	5332(1)	6547(3)	32(1)
C(15)	8285(3)	5745(1)	5811(3)	41(1)
C(16)	9959(2)	3850(1)	7736(2)	19(1)
C(17)	10542(3)	3639(1)	7092(2)	25(1)
C(18)	10160(3)	3143(1)	6570(3)	26(1)
C(19)	9208(2)	2859(1)	6673(2)	19(1)
C(20)	8633(3)	3103(1)	7311(2)	21(1)
C(21)	8998(2)	3595(1)	7858(2)	20(1)
C(22)	8392(3)	1774(1)	7116(3)	27(1)
C(23)	7375(3)	2208(1)	4582(3)	26(1)
C(24)	10078(3)	1856(1)	5872(3)	27(1)
F(1)	5833(2)	4186(1)	1622(1)	31(1)
F(2)	6743(2)	4891(1)	2629(2)	37(1)
F(3)	4712(2)	4050(1)	3156(2)	36(1)
F(4)	5801(2)	4710(1)	4191(2)	46(1)
F(5)	6684(2)	3483(1)	3541(2)	48(1)
F(6)	6816(2)	3805(1)	5160(2)	48(1)

F(7)	7898(2)	4134(1)	4339(2)	66(1)
F(8)	8028(2)	4738(1)	7014(2)	32(1)
F(9)	8834(2)	5408(1)	8202(2)	29(1)
F(10)	9326(3)	4963(1)	5806(2)	61(1)
F(11)	10345(2)	5585(1)	7043(2)	51(1)
F(12)	7194(3)	5539(1)	5370(3)	115(2)
F(13)	8289(3)	6150(1)	6458(2)	71(1)
F(14)	8517(3)	5933(1)	4956(2)	88(1)
Si(1)	6314(1)	7428(1)	3752(1)	18(1)
Si(2)	8755(1)	2163(1)	6044(1)	19(1)
Cl(1)	1907(1)	5619(1)	120(1)	23(1)
Cl(2)	12729(1)	3954(1)	10090(1)	23(1)
I(1)	4010(1)	5027(1)	1326(1)	18(1)
I(2)	10681(1)	4561(1)	8686(1)	18(1)

Table 5. Crystal data and structure refinement for **2•HCl**.

Identification code	shelx	
Empirical formula	C _{8.50} H _{5.75} Cl F ₃ I N _{0.25} O ₂	
Formula weight	362.73	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	C c	
Unit cell dimensions	a = 18.8002(13) Å	a = 90°.
	b = 16.2335(11) Å	b = 108.8840(10)°.
	c = 15.7805(11) Å	g = 90°.
Volume	4556.9(5) Å ³	
Z	16	
Density (calculated)	2.115 Mg/m ³	
Absorption coefficient	3.067 mm ⁻¹	
F(000)	2744	
Crystal size	0.200 x 0.100 x 0.080 mm ³	
Theta range for data collection	1.698 to 25.437°.	
Index ranges	-22<=h<=22, -19<=k<=19, -19<=l<=19	
Reflections collected	52041	
Independent reflections	8303 [R(int) = 0.0373]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.7452 and 0.5911	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	8303 / 2 / 573	
Goodness-of-fit on F ²	1.126	
Final R indices [I>2sigma(I)]	R1 = 0.0280, wR2 = 0.0684	
R indices (all data)	R1 = 0.0291, wR2 = 0.0692	
Absolute structure parameter	-0.040(6)	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.879 and -0.897 e.Å ⁻³	

Table 6. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2•HCl**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	4580(5)	11347(5)	6673(6)	21(2)
C(2)	3799(4)	9978(5)	7410(5)	17(2)
C(3)	3893(5)	10038(5)	8311(5)	22(2)
C(4)	4145(5)	9356(5)	8858(5)	25(2)
C(5)	4297(5)	8623(5)	8493(6)	27(2)
C(6)	4183(4)	8575(5)	7585(5)	21(2)
C(7)	3924(4)	9247(5)	7017(5)	18(2)
C(8)	3791(5)	9169(5)	6032(6)	22(2)
C(9)	5510(5)	8627(6)	5081(6)	25(2)
C(10)	6592(5)	7459(5)	4471(5)	19(2)
C(11)	6630(5)	6641(5)	4737(6)	21(2)
C(12)	6661(5)	6033(5)	4143(6)	25(2)
C(13)	6645(6)	6254(5)	3297(6)	29(2)
C(14)	6603(5)	7061(5)	3023(6)	22(2)
C(15)	6559(4)	7690(4)	3609(5)	15(2)
C(16)	6519(5)	8567(5)	3323(6)	21(2)
C(17)	4448(5)	6101(5)	3846(6)	25(2)
C(18)	3387(4)	4870(5)	2503(6)	18(2)
C(19)	3401(5)	4956(5)	1639(6)	24(2)
C(20)	3427(5)	4251(6)	1155(6)	24(2)
C(21)	3411(5)	3486(6)	1511(6)	27(2)
C(22)	3393(5)	3419(5)	2385(6)	19(2)
C(23)	3391(4)	4108(5)	2900(5)	16(2)
C(24)	3398(4)	4001(4)	3869(5)	12(2)
C(25)	5615(5)	3692(6)	2650(6)	29(2)
C(26)	6593(5)	2467(5)	4083(5)	18(2)
C(27)	6451(5)	1672(5)	3766(6)	22(2)
C(28)	6353(5)	1064(5)	4342(6)	24(2)
C(29)	6426(5)	1253(5)	5210(6)	24(2)
C(30)	6585(5)	2066(5)	5517(6)	21(2)

C(31)	6666(4)	2687(5)	4957(5)	15(2)
C(32)	6766(5)	3555(5)	5281(6)	20(2)
C(33)	5035(5)	3603(6)	5440(6)	26(2)
C(34)	5079(6)	4222(7)	6114(8)	43(3)
O(1)	3819(4)	9718(3)	5544(4)	26(1)
O(2)	3648(3)	8382(3)	5771(4)	22(1)
O(3)	6360(4)	9122(3)	3761(4)	26(1)
O(4)	6619(3)	8679(3)	2548(4)	21(1)
O(5)	3565(4)	4560(3)	4392(4)	26(1)
O(6)	3227(4)	3249(3)	4020(4)	24(1)
O(7)	6651(5)	4124(4)	4768(5)	41(2)
O(8)	6944(3)	3629(4)	6149(4)	22(1)
F(1)	4864(3)	11969(3)	7219(4)	28(1)
F(2)	4574(3)	11536(3)	5860(3)	28(1)
F(3)	5010(3)	10696(3)	6956(4)	29(1)
F(4)	5419(3)	9434(3)	5018(3)	30(1)
F(5)	5205(3)	8352(4)	5671(4)	39(1)
F(6)	5155(3)	8300(3)	4292(4)	30(1)
F(7)	4742(3)	6685(3)	3496(4)	39(1)
F(8)	4561(3)	6286(4)	4695(4)	36(1)
F(9)	4787(3)	5395(3)	3809(4)	35(1)
F(10)	5557(3)	4498(3)	2766(4)	41(1)
F(11)	5339(3)	3548(4)	1793(4)	44(2)
F(12)	5226(3)	3318(4)	3071(5)	47(2)
Cl(1)	1951(1)	10453(1)	6742(1)	18(1)
Cl(2)	8301(1)	7848(1)	5948(1)	18(1)
Cl(3)	1666(1)	5515(1)	2015(1)	18(1)
Cl(4)	8344(1)	2751(1)	3879(1)	20(1)
I(1)	3433(1)	11070(1)	6674(1)	16(1)
I(2)	6712(1)	8313(1)	5527(1)	15(1)
I(3)	3238(1)	5990(1)	3110(1)	16(1)
I(4)	6804(1)	3305(1)	3157(1)	16(1)
N(1)	4993(5)	3120(5)	4904(6)	37(2)

Table 7. Crystal data and structure refinement for **1•HCl**.

Identification code	shelx	
Empirical formula	C ₁₀ H ₁₁ Cl F ₃ I O	
Formula weight	366.54	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/n	
Unit cell dimensions	a = 8.1777(4) Å	a = 90°.
	b = 17.9834(8) Å	b = 115.8250(10)°.
	c = 8.8898(4) Å	g = 90°.
Volume	1176.79(9) Å ³	
Z	4	
Density (calculated)	2.069 Mg/m ³	
Absorption coefficient	2.963 mm ⁻¹	
F(000)	704	
Crystal size	0.100 x 0.080 x 0.040 mm ³	
Theta range for data collection	2.265 to 25.379°.	
Index ranges	-9<=h<=9, -21<=k<=21, -10<=l<=10	
Reflections collected	23541	
Independent reflections	2156 [R(int) = 0.0482]	
Completeness to theta = 25.000°	99.9 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.745 and 0.590	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2156 / 0 / 148	
Goodness-of-fit on F ²	1.319	
Final R indices [I>2sigma(I)]	R1 = 0.0376, wR2 = 0.0784	
R indices (all data)	R1 = 0.0401, wR2 = 0.0793	
Extinction coefficient	n/a	
Largest diff. peak and hole	0.993 and -0.655 e.Å ⁻³	

Table 8. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1•HCl**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	3452(7)	3390(3)	4385(7)	13(1)
C(2)	4181(8)	3899(3)	5731(7)	14(1)
C(3)	6049(8)	3950(3)	6508(7)	18(1)
C(4)	7160(8)	3553(3)	5979(7)	20(1)
C(5)	6411(8)	3074(4)	4616(7)	20(1)
C(6)	4544(8)	2996(3)	3824(7)	18(1)
C(7)	3016(8)	4374(3)	6307(7)	17(1)
C(8)	2262(8)	3912(3)	7322(7)	16(1)
C(9)	4062(10)	5045(4)	7369(8)	26(2)
O(1)	1531(6)	4653(2)	4827(5)	22(1)
I(1)	657(1)	3129(1)	3067(1)	13(1)
F(1)	-968(5)	4503(2)	1099(4)	27(1)
F(2)	1853(5)	4399(2)	1658(4)	28(1)
F(3)	-134(5)	3726(2)	-263(4)	25(1)
C(10)	308(8)	4022(3)	1232(7)	18(1)
Cl(1)	1541(2)	2018(1)	5558(2)	19(1)

Table 9. Crystal data and structure refinement for **1•AcCl**

Identification code	shelx	
Empirical formula	C ₁₂ H ₁₃ Cl F ₃ I O ₂	
Formula weight	408.57	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 11.2059(11) Å	a = 90°.
	b = 13.8263(13) Å	b = 94.868(2)°.
	c = 9.0501(9) Å	g = 90°.
Volume	1397.1(2) Å ³	
Z	4	
Density (calculated)	1.942 Mg/m ³	
Absorption coefficient	2.512 mm ⁻¹	
F(000)	792	
Crystal size	0.200 x 0.080 x 0.080 mm ³	
Theta range for data collection	1.824 to 25.388°.	
Index ranges	-13<=h<=13, -16<=k<=16, -10<=l<=10	
Reflections collected	53119	
Independent reflections	2574 [R(int) = 0.0503]	
Completeness to theta = 25.000°	100.0 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.8620 and 0.7420	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2574 / 0 / 175	
Goodness-of-fit on F ²	1.138	
Final R indices [I>2sigma(I)]	R1 = 0.0262, wR2 = 0.0623	
R indices (all data)	R1 = 0.0300, wR2 = 0.0647	
Extinction coefficient	n/a	
Largest diff. peak and hole	1.774 and -0.361 e.Å ⁻³	

Table 10. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **1•AcCl**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	$U(\text{eq})$
C(1)	6728(3)	3710(2)	3150(3)	14(1)
C(2)	5648(3)	3222(2)	3008(3)	16(1)
C(3)	4921(3)	3271(2)	1692(4)	17(1)
C(4)	5311(3)	3808(2)	532(3)	16(1)
C(5)	6402(3)	4293(2)	705(3)	16(1)
C(6)	7150(3)	4281(2)	2025(3)	14(1)
C(7)	8328(3)	4849(2)	2108(3)	15(1)
C(8)	8477(3)	5480(2)	753(3)	20(1)
C(9)	9422(3)	4202(2)	2323(4)	18(1)
C(10)	6731(3)	4593(2)	6286(3)	18(1)
C(11)	7728(3)	6253(2)	3512(4)	23(1)
C(12)	8155(4)	6876(3)	4802(4)	33(1)
F(1)	6227(2)	5195(1)	5267(2)	21(1)
F(2)	7468(2)	5109(1)	7206(2)	23(1)
F(3)	5872(2)	4233(1)	7043(2)	26(1)
Cl(1)	8615(1)	1883(1)	3526(1)	19(1)
I(1)	7690(1)	3415(1)	5232(1)	14(1)
O(1)	6892(2)	6444(2)	2629(3)	26(1)
O(2)	8412(2)	5460(2)	3476(2)	19(1)

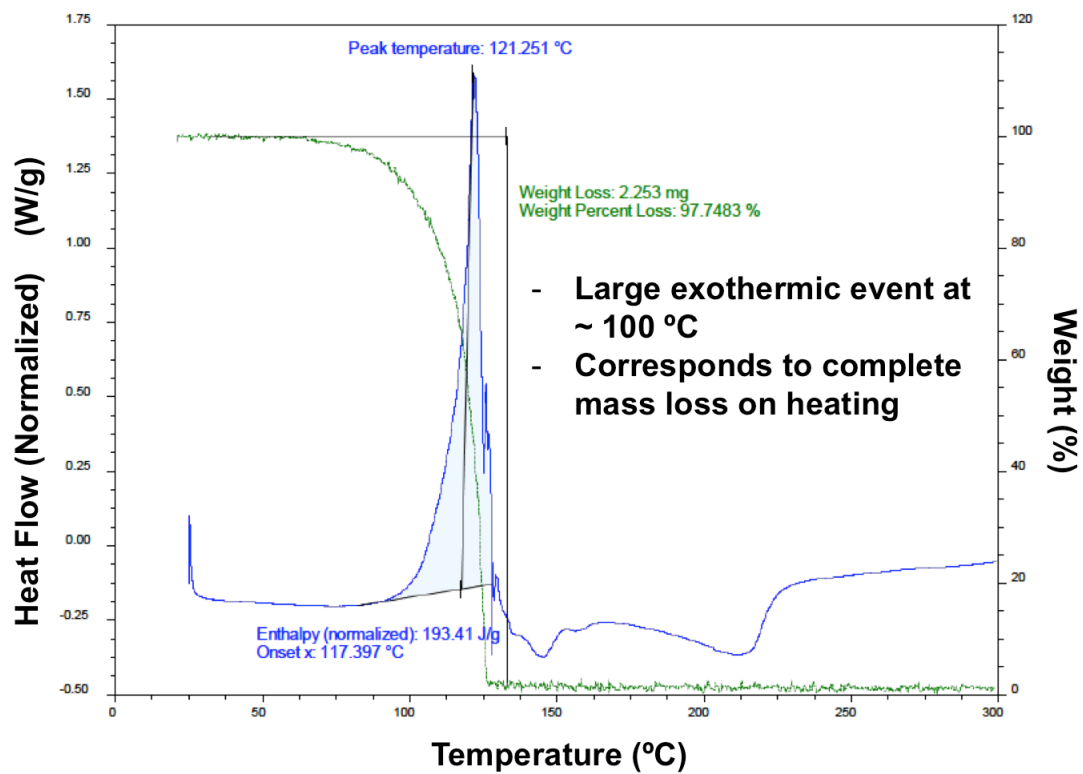
Table 11. Crystal data and structure refinement for **2•MeCl**.

Identification code	AVS7020	
Empirical formula	C ₉ H ₇ Cl F ₃ I O ₂	
Formula weight	366.50	
Temperature	100(2) K	
Wavelength	0.71073 Å	
Crystal system	Monoclinic	
Space group	P 21/c	
Unit cell dimensions	a = 6.4617(2) Å b = 18.6546(7) Å c = 9.1924(4) Å	a = 90°. b = 94.8330(10)°. g = 90°.
Volume	1104.12(7) Å ³	
Z	4	
Density (calculated)	2.205 Mg/m ³	
Absorption coefficient	3.165 mm ⁻¹	
F(000)	696	
Crystal size	0.160 x 0.160 x 0.040 mm ³	
Theta range for data collection	2.183 to 25.352°.	
Index ranges	-7 ≤ h ≤ 7, -22 ≤ k ≤ 20, -11 ≤ l ≤ 9	
Reflections collected	8551	
Independent reflections	2004 [R(int) = 0.0785]	
Completeness to theta = 25.000°	99.8 %	
Absorption correction	Semi-empirical from equivalents	
Max. and min. transmission	0.490 and 0.388	
Refinement method	Full-matrix least-squares on F ²	
Data / restraints / parameters	2004 / 0 / 146	
Goodness-of-fit on F ²	1.059	
Final R indices [I > 2σ(I)]	R1 = 0.0376, wR2 = 0.0998	
R indices (all data)	R1 = 0.0390, wR2 = 0.1013	
Extinction coefficient	n/a	
Largest diff. peak and hole	2.712 and -2.056 e.Å ⁻³	

Table 12. Atomic coordinates ($\times 10^4$) and equivalent isotropic displacement parameters ($\text{\AA}^2 \times 10^3$) for **2•MeCl**. $U(\text{eq})$ is defined as one third of the trace of the orthogonalized U_{ij} tensor.

	x	y	z	U(eq)
C(1)	5048(6)	6608(2)	3389(4)	17(1)
C(2)	3139(7)	6927(2)	3005(5)	19(1)
C(3)	2136(6)	6785(2)	1643(5)	21(1)
C(4)	3037(6)	6338(2)	687(4)	22(1)
C(5)	4932(6)	6008(2)	1088(4)	20(1)
C(6)	5970(6)	6132(2)	2463(4)	17(1)
C(7)	7978(6)	5755(2)	2900(4)	20(1)
C(8)	10369(6)	4889(2)	2258(5)	29(1)
C(9)	4472(6)	6101(2)	6442(4)	21(1)
O(1)	9018(5)	5846(2)	4016(3)	34(1)
O(2)	8480(4)	5286(2)	1886(3)	24(1)
F(1)	2751(4)	6408(2)	6823(4)	49(1)
F(2)	3925(4)	5590(1)	5513(3)	40(1)
F(3)	5419(4)	5799(2)	7608(3)	42(1)
Cl(1)	8384(1)	7885(1)	3671(1)	21(1)
I(1)	6458(1)	6912(1)	5460(1)	14(1)

DSC and TGA data for 1•HCl



Cyclic Voltammograms of 1•HCl and 2•HCl

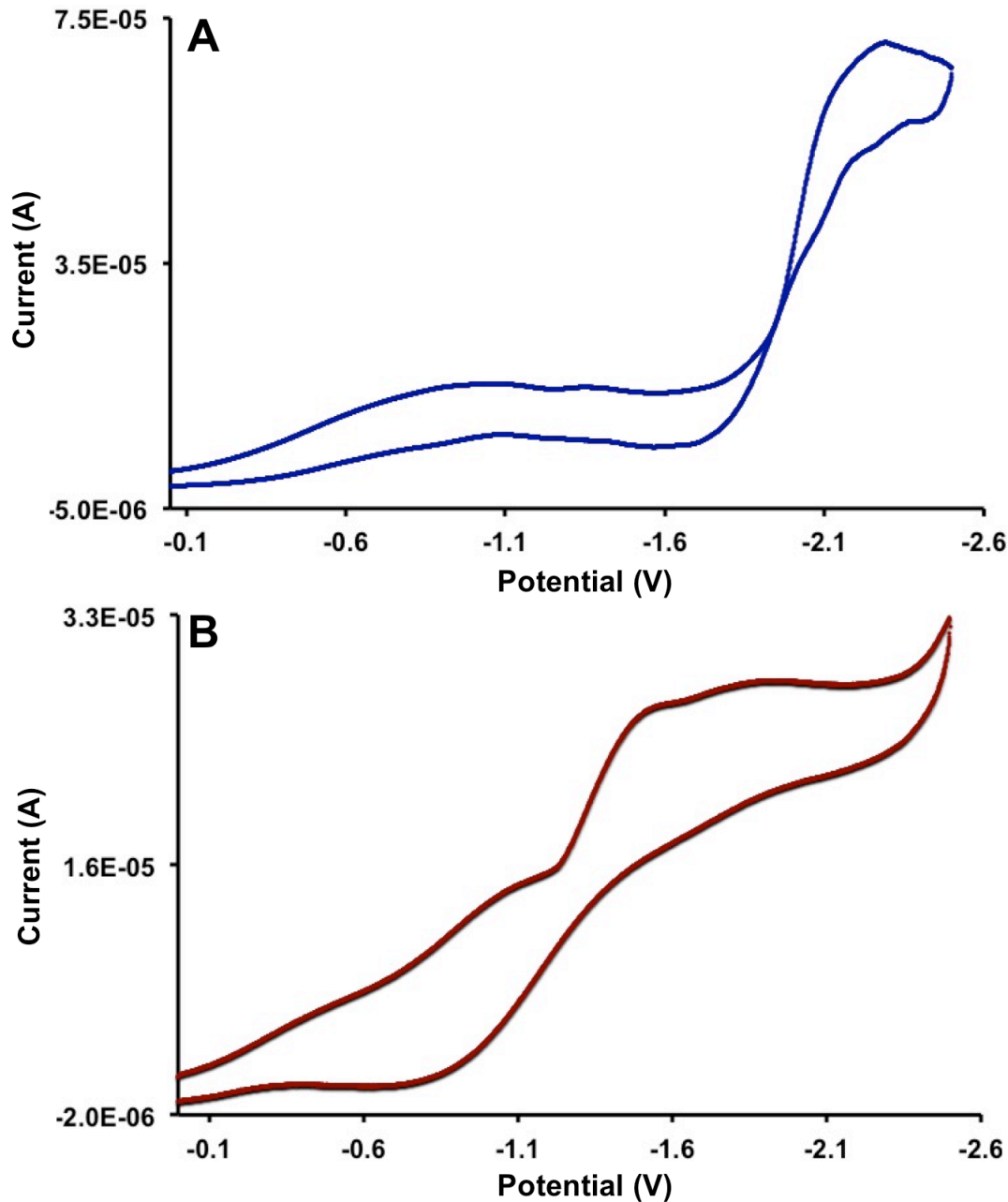


Figure S2. Cyclic voltammetry experiments. (A) Cyclic voltammogram of 1•HCl in MeCN ([1•HCl] = 1 mM). Potentials are referenced against Ag/AgNO₃. (B) Cyclic voltammogram of 2•HCl in MeCN ([2•HCl] = 1 mM). Potentials are referenced against Ag/AgNO₃.